## Supporting Information

## for

## Remarkable effect of $\pi$ -skeleton conformation in finitely conjugated polymer semiconductors

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**Fig. S1** High-temperature gel permeation chromatography (HT-GPC) plots of the TFEcontaining finitely conjugated polymers, (a) **PNBDO-T**, (b) **PNBDO-BiT**, and (c) **PNBDO-TriT**.

**Table S1** Molecular weight and distribution of the TFE-containing finitely conjugated

 polymers<sup>a)</sup>

	$M_{ m p}$	M <sub>n</sub>	$M_{ m v}$	$M_{ m w}$	$M_{\rm z}$	<i>M</i> <sub>z</sub> +1	Đ
PNBDO-T	80484	55914	86495	93335	150074	219256	1.6693
PNBDO-BiT	102766	65227	131983	147906	291618	475939	2.2676
PNBDO-TriT	78540	72664	139389	153873	276069	420239	2.1176

<sup>a)</sup> GPC versus polystyrene standards in 1,2,4-trichlorobenzene at 150 °C.

Table S2 UPS spectra parameters of polymer thin films<sup>a)</sup>

polymer	$E_{cutoff}$ (eV)	E <sub>H, onset</sub> (eV)	IP (eV)
PNBDO-T	16.93	1.60	5.89
PNBDO-BiT	16.89	1.49	5.82
PNBDO-TriT	16.94	1.36	5.62

a) IP =  $hv - (E_{cutoff} - E_{H, onset}), hv = 21.22 \text{ eV}.$ 



Fig. S2 TGA traces of the TFE-containing finitely conjugated polymers, PNBDO-T, PNBDO-BiT, and PNBDO-TriT.



**Fig. S3** DSC curves of the TFE-containing finitely conjugated polymers, (a) **PNBDO-T**, (b) **PNBDO-BiT**, and (c) **PNBDO-TriT**.



**Fig. S4** Temperature-dependent absorption profiles of the TFE-containing finitely conjugated polymers, (a) **PNBDO-T**, (b) **PNBDO-BiT**, and (c) **PNBDO-TriT**, in dilute chlorobenzene solution.



**Fig. S5** Transfer characteristics ( $V_{DS} = -40$  and 40V) and output characteristics of flexible FETs based on **PNBDO-T**.



Fig. S6 Transfer characteristics ( $V_{DS} = -40$  and 40V) and output characteristics of flexible FETs based on **PNBDO-TriT**.



Fig. S7 Mobility versus gate voltage characteristics.



**Fig. S8** Normalized annealing temperature-dependent electron mobilities of (a) **PNBDO-T-**, (b) **PNBDO-BiT-**, and (c) **PNBDO-TriT**-based FETs.



Fig. S9 AFM height images of the as-spun polymer thin films spin-coated on PET substrate, (a) PNBDO-T, (b) PNBDO-BiT, and (c) PNBDO-TriT (3  $\mu$ m × 3  $\mu$ m).



**Fig. S10** 2D-GIXRD diffraction pattern of the as-spun polymer thin films spin-coated on SiO<sub>2</sub>/Si substrate, (a) **PNBDO-T**, (b) **PNBDO-BiT**, and (c) **PNBDO-TriT**.



**Fig. S11** 1D-GIXRD diffraction pattern of the as-spun polymer thin films spin-coated on SiO<sub>2</sub>/Si substrate: (a, c, and e) out-of-plane and (b, d, and f) in plane, (a, b) **PNBDO-T**, (c, d) **PNBDO-BiT**, and (e, f) **PNBDO-TriT**.

## <sup>1</sup>H and <sup>13</sup>C NMR spectra









